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PROVISIONAL APPLICATION COVER SHEET

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TITLE OF THE INVENTION (280 characters max)

PROCESS FOR PREPARING 1,3-DIBROMOACETONE, 1,3-DICHLOROACETONE AND EPICHLOROHYDRIN

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PROVISIONAL APPLICATION FILING ONLY

PROCESS FOR PREPARING 1,3-DIBROMOACETONE, 1,3-DICHLOROACETONE AND EPICHLOROHYDRIN

Background of the Invention

The present invention relates to the art of making 1,3-dibromoacetone, 1,3-dichloroacetone and epichlorohydrin.

1,3-Dibromoacetone belongs to the class of 1,3-dihaloacetones which includes dichloroacetone and difluoroacetone. These dihaloacetone derivatives have been shown to be useful for making intermediates for pharmaceuticals and fine chemicals as well as industrial chemicals including epichlorohydrin. However, there is currently a need for the preparation of 1,3-dihaloacetone derivatives in high yield. The preparation of 1,3-dichloroacetone directly from the reaction of acetone with chlorine produces excessive amounts of 1,1-dichloroacetone as well as trichloroacetone derivatives. It has been proposed that 1,3-dichloroacetone can be made selectively by reaction of acetone with chlorine. For example, Kurkov (U.S. Pat. No. 4,251,467 (Feb. 17, 1981)) proposed making 1,3-dichloroacetone by the reaction of acetone and chlorine in the presence of iodine containing compound. The costs associated with this process are high due to the high cost of iodine and the production of large amounts of unwanted chlorinated byproducts.

1,3-Dibromoacetone is difficult to prepare in high yield since direct bromination of acetone or bromination of bromoacetone leads to multiple products. V.P. Kutrov and A.N. Koskyuk (SU 1,567,568) describe the preparation of 1,3-dibromoacetone by reacting acetone with two molar equivalents of bromine to give a mixture of brominated acetone products. This mixture of brominated acetone products was treated with sodium bisulfite, the sodium bisulfite adduct of 1,3-dibromoacetone was isolated by filtration and then the sodium bisulfite adduct of 1,3-dibromoacetone was decomposed with sulfuric acid. 1,3-Dibromoacetone was isolated from the sulfuric acid solution by filtration and then purified by recrystallization. This process is complex requiring multiple chemical steps, gives 1,3-dibromoacetone in low

yield and produces a large amount of brominated acetones derivatives and hydrogen bromide as waste products.

It would be desirable to provide a commercially feasible and effective process for the preparation of 1,3-dibromoacetone and 1,3-dichloroacetone.

Summary of the Invention

In a first aspect, the present invention is a process for preparing 1,3-dibromoacetone which comprises:

1) reacting acetone with bromine to make a mixture of brominated acetone derivatives and hydrogen bromide byproduct, and

2) equilibrating the mixture of brominated acetone derivatives and hydrogen bromide to produce 1,3-dibromoacetone as the major product.

In a second aspect, the present invention is a process which comprises:

1) isolating the 1,3-dibromoacetone from the mixture of brominated acetone derivatives produced by the process of the first aspect, and

2) equilibrating the remaining mixture of brominated acetone derivatives with hydrogen bromide to produce 1,3-dibromoacetone as the major product

In a third aspect, the present invention is a process which comprises:

1) converting to bromine the hydrogen bromide byproduct produced by the process of the first aspect, and

2) recycling the recovered bromine for use in the acetone bromination reaction.

In a fourth aspect, the present invention is a process for preparing 1,3-dichloroacetone which comprises:

1) reacting acetone with bromine to produce a mixture of major product 1,3-dibromoacetone and byproduct hydrogen bromide;

2) reacting the 1,3-dibromoacetone with a chloride source to produce a mixture of major product 1,3-dichloroacetone and byproduct bromide; and

3) isolating the 1,3-dichloroacetone.

In a fifth aspect, the present invention is a process for preparing epichlorohydrin which comprises

1) reacting acetone with bromine to produce a mixture of 1,3-dibromoacetone major product and hydrogen bromide byproduct;

2) reacting the 1,3-dibromoacetone with a chloride source to produce 1,3-dichloroacetone and a bromide byproduct;

(3) hydrogenating the 1,3-dichloroacetone in the presence of a catalyst to produce 1,3-dichlorohydrin; and

(4) cyclizing the 1,3-dichlorohydrin with a base to produce epichlorohydrin.

In a sixth aspect, the present invention is a process which comprises:

1) reacting acetone with bromine to produce a mixture of 1,3-dibromoacetone major product and a bromide byproduct;

2) reacting a chloride source with the 1,3-dibromoacetone to produce a mixture of 1,3-dichloroacetone, and a bromide byproduct;

3) converting to bromine the byproduct bromide produced in step 2), and

4) recycling the bromine to the acetone-bromination reaction and the chloride source to the 1,3-dichloroacetone reaction.

In a seventh aspect, the present invention is a process which comprises preventing or minimizing the formation of large amounts of tetrabromoacetone by thoroughly mixing the bromine and the acetone before the addition of a catalyst or the reaction self-initiates.

In an eighth aspect, the present invention is a process which comprises increasing the conversion of 1,3-dibromoacetone above its equilibrium concentration in a mixture of bromoacetone derivatives by crystallizing 1,3-dibromoacetone in the presence of a catalyst that interconverts the brominated acetone mixture.

In a ninth aspect, the present invention is a process which comprises isolating the 1,3-dibromoacetone from the mixture of brominated acetone derivatives produced by the process of the first aspect by distillation.

In a tenth aspect, the present invention is a process which comprises increasing the yield of 1,3-dibromoacetone by treating the brominated acetone derivatives produced by the process of the first aspect with a catalyst that interconverts the brominated acetone derivatives to 1,3-dibromoacetone.

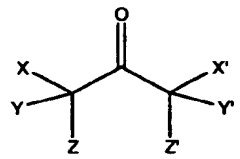
In an eleventh aspect, the present invention is a process which comprises increasing the yield of 1,3-dibromoacetone by recombining and equilibrating in the presence of a catalyst the brominated acetone derivatives isolated from the reaction mixture of the process of the first aspect to give a mixture containing 1,3-dibromoacetone as the major product.

Other aspects of the present invention will become apparent from the following detailed description and claims.

Detailed Description of the Invention

The bromoacetone derivatives formed in the acetone bromination step are represented by Formula I as follows:

Formula I



wherein X is bromine, Z and Z' are hydrogen, Y, Y' and X' are individually hydrogen or bromine.

The reactions of bromine with acetone to produce monobromoacetone and bromoacetone with bromine to produce a mixture of products including 1,3-dibromoacetone are known. See, for example, C. Rappe Arkiv. For Kemi, 21(46), 1963, 502-512 and references cited therein. The reaction of acetone with 2 molar equivalents in an aqueous solution to give a mixture of products including 1,3-dibromoacetone has also been described: J. Wielgar, Z. Domagala and R. Kolinski, Journal of Flourine Chemistry, 35, 1987, 643-652. These references describe isolation of 1,3-dibromoacetone from the reaction product mixture by fractional distillation.

An equilibration reaction catalyzed by hydrogen bromide can interconvert the products from dibromination of acetone to give a mixture where 1,3-dibromoacetone is the major product in a mixture containing acetone, monobromoacetone, 1,1-dibromoacetone and tribromoacetone with varying amounts of higher brominated products. The equilibration reaction limits the concentration of 1,3-dibromoacetone in the dibrominated acetone solution to a maximum concentration of about 70%. The equilibrium of 1,3-dibromoacetone with bromoacetone, 1,1-dibromoacetone and tribromoacetone was demonstrated by treatment of 1,3-dibromoacetone with hydrogen bromide in diethyl ether. The resulting solution contained 6% bromoacetone, 6% 1,1-dibromoacetone, 70% 1,3-dibromoacetone and 17% tribromoacetone.

The bromination of acetone to produce a mixture of dibromoacetone can be conducted in organic or aqueous solvents provided the solvents are inert to the effects of bromine and hydrogen bromide. Examples of suitable solvents include chlorinated methane solvents such as dichloromethane, chloroform, carbon tetrachloride; ether solvents including dialkyl ethers and dioxane; and ester solvents including ethyl acetate. The bromination reaction can also be performed using the equilibrated dibromoacetone mixture as the solvent. Solvents that have low solubility for the reactants or products such as hexane are not preferred since

the brominated acetone products form a second phase under some conditions resulting in lower acetone conversion.

The temperature of the reaction is not critical, provided that all of the reagents remain liquid and in contact with each other in a single phase. However, low temperatures may require addition of hydrogen bromide or other acid catalyst to initiate the reaction in a useful time. The reaction temperature is preferably at least about -10°C., more preferably at least about 10°C. The reaction temperature is preferably less than about 150°C., more preferably no more than about 100°C and, most preferably no more than about 85°C.

The reaction pressure must be high enough to ensure there is sufficient hydrogen bromide or other suitable acid present to catalyze the reaction of bromine with acetone and the equilibrium of the brominated acetone products in a useful time. The pressure is preferably at least about 7 psi (48.5 kPa, 0.5 atmosphere) and more preferably at least about 14 psi (97 kPa, 1 atmospheres). The pressure is preferably no more than about 3,000 psi (21 MPa, 220 atmospheres).

The mole ratio of bromine to acetone is preferably between 1.5 and 2.5 moles of bromine for every mole of acetone, more preferably between 1.9 and 2.1 moles of bromine for every mole of acetone, and most preferably 2 moles of bromine for every mole of acetone.

It has been found that the formation of higher brominated acetone derivatives such as tetrabromoacetone can be reduced by the rapid mixing of bromine and acetone such that the reaction mass is well mixed before the reaction begins. The reaction of bromine and acetone is autocatalytic since the hydrogen bromide formed as a byproduct catalyzes the reaction. Rapid mixing of acetone and bromine prior to the introduction or spontaneous formation of hydrogen bromide catalyst results in significantly lower tetrabromoacetone concentrations. The acetone and bromine may be premixed before introduction of solvent. The reaction can be conducted using continuous reactors.

Surprisingly, it has also been found that cooling a solution of the dibromoacetone mixture in the presence of hydrogen bromide results in formation of crystalline 1,3-dibromoacetone. Crystalline 1,3-dibromoacetone does not undergo the equilibration reaction while the other dibromoacetone product mixture continues to equilibrate to maintain the concentration of 1,3-dibromoacetone in the liquid phase. The concentration of 1,3-dibromoacetone in the overall contents including both crystallized 1,3-dibromoacetone and the equilibrium solution can be increased to greater than 95%. The limitations of the equilibrium concentration of the dibrominated acetone mixture can be overcome also by the removal of crystalline 1,3-dibromoacetone from the brominated acetone mixture by filtration. The concentration of 1,3-dibromoacetone in the liquid phase can be maintained by equilibration in the presence of hydrogen bromide. Removal of crystalline 1,3-dibromoacetone allows conversion of the other materials present in the equilibrium to 1,3-dibromoacetone in high yield.

The limitation of the formation of an equilibrium concentration of 1,3-dibromoacetone can be overcome by isolation of 1,3-dibromoacetone by crystallization or fractional distillation or a combination of these techniques. The other brominated acetone derivatives isolated from the reaction mixture including bromoacetone, 1,1-dibromoacetone and tribromoacetone, can be recombined and equilibrated to give 1,3-dibromoacetone as the major product. This can be repeated until essentially complete conversion to 1,3-dibromoacetone is achieved.

The present invention also encompasses the preparation of 1,3-dichloroacetone from 1,3-dibromoacetone by reacting 1,3-dibromoacetone with a chloride source such as, for example, lithium chloride, sodium chloride, potassium chloride, magnesium chloride, calcium chloride, manganese chloride, zinc chloride, hydrogen chloride, ammonium chloride, tetramethylammonium chloride, tetraethylammonium chloride, Dowex Marathon MSA ion exchange Resin and poly(4-

vinylpyridine), cross-linked, methyl chloride quaternary salt. Other suitable chloride sources include inorganic ionic chlorides and organic chlorides including amine hydrochloride salts, quaternary ammonium salts and phosphonium chloride salts and combinations thereof.

The chloride source is employed in a chloride source to dibromoacetone mole ratio of from 0.1 to 200, preferably from 1 to 100 and, most preferably from 2 to 75. The reaction of 1,3-dibromoacetone with a chloride source can be repeated to increase conversion.

The solvents which can be employed in the present invention include, for example, water, organic solvents such as, for example, alcohols, ethers, esters, ketones, chlorinated hydrocarbons and combinations thereof.

The reaction can be carried out in the absence or presence of a solvent. The reaction temperature is not critical, but, in general, the reaction temperature is from 0°C to about 200°C, preferably from about 10°C to about 175°C and, most preferably from about 20°C to about 150°C.

If employed, the solvent can be used in an amount up to 99% by weight.

The reaction pressure is also not critical but, in general, the reaction pressure is from vacuum to about 3000 psig.

The reaction can be conducted using continuous and/or fixed bed reactors.

The product 1,3-dichloroacetone can be recovered from the chloride source that contains the bromide byproduct by known methods such as extraction or distillation.

A key feature of the present invention is to convert the byproducts hydrogen bromide and/or bromide salts to bromine for recycle. The conversion of hydrogen bromide to bromine is well known. See for example Schubert et al, Chemtech, April 1993, pages 37-41. Hydrogen bromide can be converted to bromine by oxidants such as oxygen, including air, chlorine and hydrogen peroxide. Hydrogen bromide can be

converted to an aqueous solution of hydrobromic acid and the hydrobromic acid oxidized to bromine. The hydrogen bromide can be neutralized to form bromides salts. Treatment of bromide salts with chlorine to produce bromine and chloride salts is currently practiced commercially. The chloride salts or hydrogen chloride resulting from the recovery of bromine may be recycled to the reaction of 1,3-dibromoacetone with a chloride source.

The following working examples are given to illustrate the invention and should not be construed as limiting its scope. Unless otherwise indicated, all parts and percentages are by weight and product analysis is by gas chromatography area percent.

EXAMPLE 1 ACETONE BROMINATION IN ETHYL ACETATE WITH RAPID MIXING OF ACETONE AND BROMINE

A 2000 ml jacketed glass reactor was equipped with a stirrer, addition funnel and a cold finger condenser charged with ice and vented to a pair of gas scrubbers charged with water. The reactor was charged with 136.6 grams of ethyl acetate and 19.5 grams of acetone and the solution was warmed to 30°C. 107.4 grams of bromine was charged to the addition funnel and then added to the reactor within 5 seconds. The reaction was complete within 45 seconds as evidenced by the disappearance of the bromine color. The reaction mixture was sparged with nitrogen for 30 minutes. Analysis of the reaction products (area % by gas chromatography) was: 13.0% bromoacetone, 5.4% 1,1-dibromoacetone, 70.5% 1,3-dibromoacetone, 11.1% tribromoacetone. Tetrabromoacetone was present at less than 0.2%.

COMPARATIVE EXAMPLE A ACETONE BROMINATION IN ETHYL ACETATE WITH BROMINE ADDITION OVER 15 MINUTES AS DESCRIBED IN SU 1,567,568

A 2000 ml jacketed glass reactor was equipped with a stirrer, addition funnel and a cold finger condenser charged with ice and vented to a pair of gas scrubbers charged with water. The reactor was charged with 136.2

grams of ethyl acetate and 31.3 grams of acetone and the solution warmed to 30°C. 170.0 grams of bromine was charged to the addition funnel and added to the acetone solution over 15 minutes. The reaction mixture was sparged with nitrogen for 30 minutes. Analysis of the reaction products (area % by gas chromatography) was 12.9% bromoacetone, 8.3% 1,1-dibromoacetone, 62.3% 1,3-dibromoacetone, 15.6% tribromoacetone and 2.4% tetrabromoacetone.

EXAMPLE 2 ACETONE BROMINATION IN DIETHYL ETHER

A 2000 ml jacketed glass reactor was equipped with a stirrer, addition funnel and a cold finger condenser charged with ice and vented to a pair of gas scrubbers charged with water. The reactor was charged with 150.0 grams of diethyl ether and 16.0 grams of acetone and the solution was stirred at 20°C. 88.4 grams of bromine was added to the addition funnel and then charged to the reactor within 5 seconds. The reaction was complete within 60 seconds as evidenced by the disappearance of the bromine color. The reaction mixture was stirred for 30 minutes. Analysis of the reaction products (area % by gas chromatography) was: 11.5% bromoacetone, 7.0% 1,1-dibromoacetone, 68.2% 1,3-dibromoacetone, 12.2% tribromoacetone and 0.2% tetrabromoacetone.

EXAMPLE 3 ACETONE BROMINATION IN BROMINATED ACETONE MIXTURE

A 2000 ml jacketed glass reactor was equipped with a stirrer, addition funnel, dip tube for gas addition and a cold finger condenser charged with dry ice/acetone and vented to a pair of gas scrubbers charged with water. The reactor was charged with 150.1 grams of a brominated acetone mixture consisting of 9.5% bromoacetone, 4.7% 1,1-dibromoacetone, 71.7% 1,3-dibromoacetone, 13.8% tribromoacetone and 0.4% tetrabromoacetone (GC area % analysis). 16.1 Grams of acetone was added to the brominated acetone mixture and the solution was stirred at 20°C. 88.7 grams of bromine was added to the addition funnel and then charged to the reactor within 5 seconds and the solution was stirred for 1 minute. A catalytic amount of hydrogen bromide was added to the

reaction mixture to initiate the reaction. The reaction was complete within 60 seconds as evidenced by the cessation of gas evolution. The reaction mixture was stirred for 90 minutes minutes. Analysis of the reaction products (area % by gas chromatography) was: 0.5% acetone, 10.0% bromoacetone, 5.0% 1,1-dibromoacetone, 69.2% 1,3-dibromoacetone, 14.9% tribromoacetone and 0.4% tetrabromoacetone. The reaction mixture was discharged into 100 grams of water, the layers separated giving 207 grams of dibromoacetone mixture.

EXAMPLE 4 ACETONE BROMINATION IN DICHLOROMETHANE

A 2000 ml jacketed glass reactor was equipped with a stirrer, dip tube for gas addition, addition funnel and a cold finger condenser charged with dry ice/acetone and vented to a pair of gas scrubbers charged with water. The reactor was charged with 155 grams of dichloromethane and 14.8 grams of acetone and the solution was stirred at 20°C. 81.3 grams of bromine was added to the addition funnel and then charged to the reactor within 5 seconds. A catalytic amount of hydrogen bromide was added after the solution was well mixed. The reaction was complete within 5 minutes of hydrogen bromide addition as evidenced by the disappearance of the bromine color. The initial product mixture was stirred for 2 hours. Analysis of the reaction products (area % by gas chromatography) was: 12.9% bromoacetone, 8.3% 1,1-dibromoacetone, 62.3% 1,3-dibromoacetone, 15.6% tribromoacetone and 0.1% tetrabromoacetone.

EXAMPLE 5 ACETONE BROMINATION IN HEXANE

A 2000 ml jacketed glass reactor was equipped with a stirrer, dip tube for gas addition, addition funnel and a cold finger condenser charged with ice and vented to a pair of gas scrubbers charged with water. The reactor was charged with 152 grams of hexane and 16.3 grams of acetone and the solution was stirred at 20°C. 89.6 grams of bromine was added to the addition funnel and then charged to the reactor within 5 seconds. After 5 minutes, a catalytic amount of hydrogen bromide was added to initiate the reaction. A second bromine

rich lower layer formed in the reaction before the bromine color dissipated within 2 minutes of hydrogen bromide addition. The reaction mixture was stirred for 30 minutes. Analysis of the products (area % by gas chromatography) was 4.3% acetone, 11.3% bromoacetone, 6.2% 1,1-dibromoacetone, 62.2% 1,3-dibromoacetone, 14.1% tribromoacetone and 0.2% tetrabromoacetone.

EXAMPLE 6 EQUILIBRATION OF DIBROMOACETONE MIXTURE DURING CRYSTALLIZATION

1,3-Dibromoacetone product mixture prepared according to Example 3????? was washed with water and the solvent removed under vacuum. Hydrogen bromide, 0.5 grams, was added to 50.2 grams of the bromination product mixture. The solution was cooled to 10°C and seeded with 1,3-dibromoacetone crystals. The suspension was held at 9°C until it was a solid mass. Analysis of the resulting material (area % by gas chromatography) was 0.4% bromoacetone, 0.3% 1,1-dibromoacetone, 97.3% 1,3-dibromoacetone and 2.1% tribromoacetone.

EXAMPLE 7 CONTINUOUS CRYSTALLIZATION OF DIBROMOACETONE MIXTURE WITH EQUILIBRATION

A 2000 ml jacketed glass reactor was equipped with a stirrer, thermometer and a dip tube for gas addition was used a crystallization vessel. Another dip tube for slurry transfer was connected to a 1000 ml jacketed glass sintered glass pressure filter by means of tubing containing a ball valve. The bottom of the pressure filter was connected by means of tubing containing a ball valve to the crystallizer to allow liquid return. The pressure filter was equipped with a vent valve and a nitrogen inlet valve. The crystallizer was charged with 2011 grams of equilibrated dibromoacetone mixture consisting of 13.0% bromoacetone, 5.3% 1,1-dibromoacetone, 67.2% 1,3-dibromoacetone and 11.0% tribromoacetone as analyzed by gas chromatography area %. 17.0 grams of hydrogen bromide was added and the solution was cooled to 11.5°C. The equilibrated mixture was seeded with 7.0 grams of 1,3-dibromoacetone. 1,3-Dibromoacetone crystals were isolated periodically by charging the slurry of 1,3-

dibromoacetone crystals in the crude dibromoacetone mixture to the pressure filter and removing the mother liquor by pressuring the filter and venting the liquid back into the crystallizer. After 24 hours, a total of 906 grams of 1,3-dibromoacetone crystals had been collected. Analysis of the remaining 1108 grams of mother liquor by gas chromatography area % was 12.8% bromoacetone, 5.0% 1,1-dibromoacetone, 67.0% 1,3-dibromoacetone and 10.5% tribromoacetone.

EXAMPLE 8 1,3-DIBROMOACETONE EQUILIBRATION

1 Gram of 1,3-dibromoacetone (purity >99%) was treated with 3 grams of 14% hydrogen bromide in diethyl ether for 24 hours. Analysis of the resulting material (area % by gas chromatography) was 9.6% bromoacetone, 7.2% 1,1-dibromoacetone, 71.2% 1,3-dibromoacetone and 12.0% tribromoacetone. This composition corresponds to a weight % composition of 6.1% bromoacetone, 6.3% 1,1-dibromoacetone, 70.3% 1,3-dibromoacetone and 17.3% tribromoacetone.

EXAMPLE 9 1,3-DIBROMOACETONE PREPARATION, ISOLATION, BYPRODUCT EQUILIBRATION AND 1,3-DIBROMOACETONE ISOLATION

A 2000 ml jacketed glass reactor was equipped with a stirrer, addition funnel, dip tube for gas addition and a cold finger condenser charged with ice and vented to a pair of gas scrubbers charge with water was charged with 150 grams of ethyl acetate and 16.5 grams of acetone and the solution was cooled to 10°C. 91.6 grams of bromine was charged to the addition funnel, was then added to the acetone solution over 5 seconds. The solution was stirred 5 minutes before addition of a catalytic amount of hydrogen bromide. The reaction mixture was sparged with nitrogen for 30 minutes after the disappearance of the bromine color. Solvent was removed under vacuum and the brominated acetone mixture was mixed with 178 grams of 21% diethyl ether/79% pentane and cooled to 5°C at which point crystals formed. The suspension was cooled to 0°C and held for 1 hour. The crystals were isolated, washed with 21% ether/79% pentane and dried to give 31.4 grams. Analysis of the crystalline product (area % by gas chromatography) was: 0.1% bromoacetone, 99.1% 1,3-

dibromoacetone and 0.7% tribromoacetone. The mother liquor from the crystallization was combined with the washes and the solvent removed under vacuum. 30 grams of 12% hydrogen bromide in ethyl acetate was added to the concentrated mother liquor and stirred at room temperature for 95 minutes. The equilibrated solution was washed with water and the solvent removed under vacuum. 98 Grams of 21% ether/79% pentane was added to the equilibrated mother liquor and the resulting solution was cooled until it became cloudy at which point it was seeded with 1,3-dibromoacetone crystals. The suspension was cooled to 0°C over an hour. The crystals were isolated, washed with 21% ether/79% pentane and dried to give 11.9 grams. Analysis of the crystalline product (area % by gas chromatography) was: 98.3% 1,3-dibromoacetone. Concentration of the mother liquor and the washes under vacuum gave 14.6 grams of brominated acetone derivatives.

EXAMPLES 10-22

General Procedure

Mix 1,3-dibromoacetone with a chloride source in a 60 ml serum bottle. Place the solution in a 60°C to 80°C water bath and stirred for 5 to 60 minutes. Cool the solution to room temperature, extract the brominated acetone derivatives with 10 milliliters of diethyl ether and analyze the ether layer by gas chromatography (area%). The results are shown in Table 1. Also shown in Table 1 are the chloride sources used and the amounts of chloride source and 1,3-dichloroacetone.

TABLE 1

Example	CHLORIDE SOURCE	Amount (g)	1,3-dibromoacetone (g)	BROMINATED ACETONE DERIVATIVES YIELD (%)		
				1,3-DBA	1,3-DCA	1-Br-3CA
10	Potassium chloride	13.8	2.0	0	95.3	4.6
11	Magnesium chloride hexahydrate	28.3	1.5	0.1	94.5	5.4
12	Lithium chloride	7.9	2.0	2.1	74.4	23.5
13	Calcium chloride dihydrate	27.2	2.0	0.3	91.1	8.6
14	Zinc chloride	25.3	2.0	78.0	2.5	19.5
15	Sodium chloride	10.8	2.0	0.1	95.1	4.8
16	Ammonium chloride	9.9	2.0	0.1	94.7	5.2
17	Tetramethyl ammonium chloride	20.3	2.0	0	99.0	1.0
18	Hydrochloric acid	18.3 of 37% conc.	2.0	3.1	71.0	25.9
19	Manganese dichloride tetrahydrate	20.0	1.0	0.2	93.0	6.8
20	Poly(4-vinylpyridine)methyl chloride	10.0	0.4	0	97.4	2.6
21	Dowex Marathon MSA	10.0	10	0	96.8	3.2

The following Examples 22-24 demonstrate the use of different chloride to 1,3-DBA mole ratios in the preparation of 1,3-dichloroacetone from 1,3-dibromoacetone and a chloride source.

EXAMPLE 22

2.0 grams of 1,3-dibromoacetone was mixed with 2.7 grams of sodium chloride (1:5 mole ratio) in 9.6 grams water in a 60 ml serum bottle. The solution was placed in an 80°C water bath and stirred for 10 minutes. The solution was cooled to room temperature, extracted with 10 ml of diethyl ether and the ether layer analyzed by gas chromatography (area %) to give: 26.0% 1,3-Dibromoacetone, 33.1% 1-bromo-3-chloroacetone and 40.9% 1,3-dichloroacetone.

EXAMPLE 23

2.0 grams of 1,3-dibromoacetone was mixed with 5.4 grams of sodium chloride (1:10 mole ratio) in 19.2 grams water in a 60 ml serum bottle. The solution was placed in an 80°C water bath and stirred for 10 minutes. The solution was

cooled to room temperature, extracted with 10 ml of diethyl ether and the ether layer analyzed by gas chromatography (area %) to give: 4.2% 1,3-Dibromoacetone, 19.6% 1-bromo-3-chloroacetone and 76.2% 1,3-dichloroacetone.

EXAMPLE 24

2.0 grams of 1,3-dibromoacetone was mixed with 8.1 grams of sodium chloride (1:15 mole ratio) in 28.8 grams water in a 60 ml serum bottle. The solution was placed in an 80°C water bath and stirred for 10 minutes. The solution was cooled to room temperature, extracted with 10 ml of diethyl ether and the ether layer analyzed by gas chromatography (area %) to give: 0.3% 1,3-dibromoacetone, 8.3% 1-bromo-3-chloroacetone and 91.4% 1,3-dichloroacetone.

The following Examples 25-27 demonstrate the use of different solvent concentrations in the preparation of 1,3-dichloroacetone from 1,3-dibromoacetone and a chloride source.

EXAMPLE 25

2.0 grams of 1,3-dibromoacetone was mixed with 10.8 grams of sodium chloride in 40 grams water in a 60 ml serum bottle. The solution was placed in an 60°C water bath and stirred for 5 minutes. The solution was cooled to room temperature, extracted with 10 ml of diethyl ether and the ether layer analyzed by gas chromatography (area %) to give: 26.6% 1,3-dibromoacetone, 37% 1-bromo-3-chloroacetone and 36.4% 1,3-dichloroacetone.

EXAMPLE 26

1.0 gram of 1,3-dibromoacetone was mixed with 5.4 grams of sodium chloride in 40 grams water in a 60 ml serum bottle. The solution was placed in a 60°C water bath and stirred for 5 minutes. The solution was cooled to room temperature, extracted with 10 ml of diethyl ether and the ether layer analyzed by gas chromatography (area %) to give: 12.1% 1,3-dibromoacetone, 47.0% 1-bromo-3-chloroacetone and 40.9% 1,3-dichloroacetone.

EXAMPLE 27

0.5 grams of 1,3-dibromoacetone was mixed with 2.7 grams of sodium chloride in 40 grams water in a 60 ml serum bottle. The solution was placed in an 60°C water bath and stirred for 5 minutes. The solution was cooled to room temperature, extracted with 10 ml of diethyl ether and the ether layer analyzed by gas chromatography (area %) to give: 39.6% 1,3-dibromoacetone, 48.1% 1-bromo-3-chloroacetone and 12.3% 1,3-dichloroacetone.

Examples 28-29 demonstrate the preparation of 1,3-dichloroacetone from 1,3-dibromoacetone and a chloride source under ambient temperature.

EXAMPLE 28

4.9 grams of 1,3-dibromoacetone was mixed with 38.4 grams of tetraethylammonium chloride in 10.0 grams water in a 60 ml serum bottle. The solution was stirred for 30 minutes at ambient temperature, extracted with 10 ml of diethyl ether and the ether layer analyzed by gas chromatography (area %) to give: 0.1% 1,3-Dibromoacetone, 4.3% 1-bromo-3-chloroacetone and 95.2% 1,3-dichloroacetone.

EXAMPLE 29

2.0 grams of 1,3-dibromoacetone was mixed with 13.8 grams of potassium chloride in 37.4 grams water in a 60 ml serum bottle. The solution was warmed slightly to melt the 1,3-dibromoacetone crystals and then stirred at ambient temperature for 22 hours. The solution was extracted with 10 ml of diethyl ether and the ether layer analyzed by gas chromatography (area %) to give: 0.1% 1,3-dibromoacetone, 3.7% 1-bromo-3-chloroacetone and 96.3% 1,3-dichloroacetone.

Examples 30-32 demonstrate the use of organic solvents in the preparation of 1,3-dichloroacetone from 1,3-dibromoacetone and a chloride source.

EXAMPLE 30

0.4 grams of 1,3-dibromoacetone was mixed with 10.0 grams of poly(4-vinylpyridne)methyl chloride quaternary salt in 10.0 grams diethyl ether in a 60 ml serum bottle. The

solution was placed in a 60°C water and stirred for 60 minutes. The solution was cooled to room temperature and the ether layer analyzed by gas chromatography (area %) to give: 0% 1,3-dibromoacetone, 5.7% 1-bromo-3-chloroacetone and 94.3% 1,3-dichloroacetone.

EXAMPLE 31

0.4 grams of 1,3-dibromoacetone was mixed with 10.0 grams of Dowex Marathon MSA in 10.0 grams diethyl ether in a 60 ml serum bottle. The solution was placed in a 60°C water and stirred for 60 minutes. The solution was cooled to room temperature and the ether layer analyzed by gas chromatography (area %) to give: 0.2% 1,3-dibromoacetone, 7.8% 1-bromo-3-chloroacetone and 92.0% 1,3-dichloroacetone.

EXAMPLE 32

0.29 grams of 1,3-dibromoacetone was mixed with 4.0 grams of calcium chloride dihydrate in 1.0 grams methanol in a 60 ml serum bottle. The solution was placed in a 60°C water and stirred for 60 minutes. The solution was cooled to room temperature and the ether layer analyzed by gas chromatography (area %) to give: 0% 1,3-dibromoacetone, 1.7% 1-bromo-3-chloroacetone, 89.6% 1,3-dichloroacetone and 8.7% derivatives from the reaction of methanol with 1,3-dichloroacetone.

EXAMPLE 33

In this example, no solvent was employed.

0.65 grams of 1,3-dibromoacetone was mixed with 10.0 grams of molten tetraethylammonium chloride in a 60 ml serum bottle. The solution was stirred at 60°C for 5 minutes. A 1 ml sample was added to 1 ml water and extracted with 2 ml diethyl ether and the ether layer analyzed by gas chromatography (area %) to give: 0% 1,3-dibromoacetone, 1.1% 1-bromo-3-chloroacetone and 98.9% 1,3-dichloroacetone.

EXAMPLE 34

This Example demonstrates multiple reactions employed in the preparation of 1,3-dichloroacetone from 1,3-dibromoacetone and a chloride source.

31.3 grams of 1,3-dibromoacetone was mixed with 217 grams potassium chloride in 557 grams water and the mixture was stirred in a 60°C bath for 10 minutes. The mixture was cooled to 20°C and extracted 6 times with 150 grams dichloromethane with recovery of dichloromethane from the dichloroacetone product between extractions by distillation under reduce pressure. The resulting dichloroacetone product was mixed with 218 grams potassium chloride in 563 grams water and the mixture was stirred in a 60°C bath for 10 minutes. The mixture was cooled to 20°C and extracted 6 times with 150 grams dichloromethane with recovery of dichloromethane from the dichloroacetone product between extractions by distillation under reduce pressure. A total of 18.0 grams (98% yield) of 1,3-dichloroacetone was recovered. Analysis of the crystalline product was >99.5% 1,3-dichloroacetone .

WHAT IS CLAIMED IS

1. A process for preparing 1,3-dibromoacetone which comprises:

1) reacting acetone with bromine to make a mixture of brominated acetone derivatives including acetone, bromoacetone, 1,1-dibromoacetone, 1,3-dibromoacetone, tribromoacetone and tetrabromoacetone and byproduct hydrogen bromide;

2) equilibrating the mixture of brominated acetone derivatives and hydrogen bromide to produce 1,3-dibromoacetone as the major product; and

3) isolating the 1,3-dibromoacetone from the mixture of brominated acetone derivatives by (a) filtration, (b)crystallization, (c) fractional distillation or (d) a combination thereof.

2. The process of Claim 1 which further comprises:

4) equilibrating the remaining brominated acetone derivatives in step 3) to produce 1,3-dibromoacetone as the major product; and

5) isolating the 1,3-dibromoacetone from the mixture of brominated acetone derivatives as in step 3).

3. The process of Claim 2 which further comprises:

6) repeating in sequential order Steps 4) and 5) until essentially complete conversion to 1,3-dibromoacetone is achieved;

7) producing 1,3-dibromoacetone as the major product by recombining and equilibrating in the presence of a catalyst the brominated acetone derivatives left after the removal of 1,3-dibromoacetone; and

8) isolating the 1,3-dibromoacetone.

4. The process of Claim 1 which comprises preventing or minimizing the formation of large amounts of tetrabromoacetone by thoroughly mixing the bromine and the

acetone before the addition of a catalyst or the reaction self-initiates.

5. The process of Claim 1 wherein the mole ratio of bromine to acetone is between 1.5 and 2.5.

6. The process of Claim 1 wherein the reaction temperature is between about -10°C and about 150°C.

7. The process of Claim 1 wherein the reaction pressure is between about 0.5 psig and about 3000 psig.

8. The process of Claim 1 wherein the solvent is the mixture of brominated acetone derivatives.

9. A process for preparing 1,3-dibromoacetone which comprises:

1) reacting acetone with bromine to make a mixture of brominated acetone derivatives including acetone, bromoacetone, 1,1-dibromoacetone, 1,3-dibromoacetone, tribromoacetone and tetrabromoacetone and byproduct hydrogen bromide;

2) equilibrating the mixture of brominated acetone derivatives and hydrogen bromide to produce 1,3-dibromoacetone as the major product; and

3) increasing the conversion of 1,3-dibromoacetone above its equilibrium concentration in a mixture of bromoacetone derivatives by (a) crystallizing the 1,3-dibromoacetone in the presence of a catalyst that interconverts the brominated acetone mixture or (b) treating the brominated acetone derivatives with a catalyst that interconverts the brominated acetone derivatives to 1,3-dibromoacetone.

10. The process of Claim 1 which further comprises recovering the hydrogen bromide formed as a byproduct in the bromination of acetone and converting the hydrogen bromide to molecular bromine.

11. The process of Claim 1 wherein the reaction is conducted using continuous reactors.

12. The process of Claim 10 which further comprises

recycling the bromine to the acetone-bromination reaction.

13. A process for preparing 1,3-dichloroacetone which comprises:

1) reacting acetone with bromine to produce a mixture of major product 1,3-dibromoacetone and byproduct hydrogen bromide;

2) isolating the 1,3-dibromoacetone;

3) reacting the 1,3-dibromoacetone with a chloride source to produce a mixture of major product 1,3-dichloroacetone and byproduct bromide; and

4) isolating the 1,3-dichloroacetone.

14. A process for preparing epichlorohydrin which comprises:

3) reacting acetone with bromine to produce a mixture of 1,3-dibromoacetone major product and hydrogen bromide byproduct;

4) reacting the 1,3-dibromoacetone with a chloride source to produce 1,3-dichloroacetone;

(3) hydrogenating the 1,3-dichloroacetone in the presence of a catalyst to produce 1,3-dichlorohydrin; and

(4) cyclizing the 1,3-dichlorohydrin with a base to produce epichlorohydrin.

15. The process of Claim 13 which further comprises converting the byproduct bromide to molecular bromine and regenerating the chloride source.

16. The process of Claim 15 which further comprises recycling the bromine to the acetone bromination reaction.

17. The process of Claim 15 which further comprises recycling the chloride source to the reaction of 1,3-dibromoacetone with a chloride source.

18. The process of Claim 13 wherein the reaction is conducted using continuous and/or fixed bed reactors.

19. The process of Claim 13 wherein the 1,3-dichloroacetone is isolated by continuous distillation or continuous extraction.

ABSTRACT

A process for preparing 1,3-dibromoacetone, 1,3-dibrmoacetone and epichlorohydrin which comprises: 1) reacting acetone with bromine to make a mixture of brominated acetone derivatives including acetone, bromoacetone, 1,1-dibromoacetone, 1,3-dibromoacetone, tribromoacetone and tetrabromoacetone and byproduct hydrogen bromide; 2) equilibrating the mixture of brominated acetone derivatives and hydrogen bromide to produce 1,3-dibromoacetone as the major product; 3) isolating the 1,3-dibromoacetone from the mixture of brominated acetone derivatives by (a) filtration, (b)crystallization, (c) fractional distillation or (d) a combination thereof; 4) reacting the 1,3-dibromoacetone with a chloride source to produce 1,3-dichloroacetone; 5)hydrogenating the isolated 1,3-dichloroacetone in the presence of a catalyst to produce 1,3-dichlorohydrin and 5) cyclizing the 1,3-dichlorohydrin with a base to produce epichlorohydrin.